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Patent application number (The Patent Office will fill this part in) 0407908.3

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The University of York Heslington YORK YO10 5DD

Patents ADP number (if you know it)

07245376004

If the applicant is a corporate body, give the country/state of its incorporation

Title of the invention

Ionic Liquids

Name of your agent (4) you have one)

Harrison Goddard Foote

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

31 St Saviourgate York YO1 8NQ GB

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Description

Claim(s)

Abstract

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Statement of inventorship and right to grant of a patent (Fatents Form 7/77)

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LIQUIDS

The present invention relates to ionic liquids and uses thereof. The invention also provides processes for the manufacture of ionic liquids.

Ionic liquids are compounds which are composed of ions but which have a melting point below ambient temperature. They can be formed when relatively large molecules are used as the base and/or the acid to form an ionic salt. By using a large base or acid, the degree of order of the resulting salt can be reduced and the melting point lowered to a point where the resultant salt is liquid at ambient temperature. The delocalisation of the charge on the ion is also an important factor in determining the melting point of the resulting salt.

Ionic liquids may be made up of anions and cations or alternatively consist of zwitterions carrying both a positive and a negative charge on the same molecule. Most commonly the ionic liquid will comprise an anion and a cation.

The prior art comprises liquids composed of a quaternary nitrogen-based ion, for example, based on a nucleus selected from quaternary ammonium cations, pyrazolium cations, imidazolium cations, triazolium cations, pyridinium cations, pyridinium cations, pyridinium cations, pyridinium cations and triazinium cations. These types of ionic liquids tend to be highly viscous and strongly absorb UV and visible light. Furthermore, the preparation of these ionic liquids involves a number of chemical steps that makes the process both time consuming and inefficient.

The inventors have provided further ionic liquids.

According to the present invention there is provided an ionic liquid comprising an anion and a cation wherein the cation is a primary, secondary or tertiary ammonium ion containing a charged nitrogen atom.

As used herein a "primary ammonium ion" is an ammonium ion in which the nitrogen has 1 carbon atom attached to it.

As used herein a "secondary ammonium ion" is an ammonium ion in which the nitrogen has 2 carbon atoms attached to it.

As used herein a "tertiary ammonium ion" is an ammonium ion in which the nitrogen has 3 carbon atoms attached to it.

According to a further aspect of the present invention there is provided an ionic liquid comprising an anion and a cation characterised in that the cation is a nitrogen-containing cation of the formula (I)

N⁺HRR'R'' (I)

in which R is a hydrocarbyl group optionally substituted with by one or more substituents selected from nitrogen-containing functional groups (including nitrile, nitro or amino or another basic nitrogen-containing functional group), thiol, alkythio, sulphonyl, thiocyanate, isothiocyanate, azido, hydrazino, halogen, alkyl optionally interrupted by one or more ether or thioether linkages, alkoxy, alkenyl, hydroxy, carbonyl (including aldehyde or ketone), carboxyl, boronate, silyl and substituted amino (e.g. mono- or di-alkylamino or alkyamido); and

R' and R", which may be the same or different, each represent H or R; or

any two or three of R, R', R" may be joined together with the N to form a cyclic group.

For the purposes of this invention hydrocarbyl includes, but is not limited to, alkyl, alkenyl, alkynyl, cyclohydrocarbyl, for example cycloalkyl, cycloalkenyl and moietics containing a combination thereof.

As used herein "alkyl" relates to both straight chain and branched alkyl radicals, for example, of 1 to 12 carbon atoms, e.g. 1, 2, 3, 4, 5, 6, 7, 8 carbon atoms including but not limited to methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tertbutyl, n-pentyl, n-hexyl, n-heptyl, n-octyl. The term alkyl also encompasses cycloalkyl radicals including but not limited to cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

The alkyl group may be substituted with one or more halogen atoms. In one class of compounds the halogen is fluorine, in another it is chlorine, in a third it is a combination of fluorine and chlorine.

"Alkoxy" relates to both straight chain and branched alkyl radicals, for example, of 1 to 12 carbon atoms, e.g. 1, 2, 3, 4, 5, 6, 7, 8 carbon atoms containing one or more oxygen atoms or hydroxyl.

The term "alkenyl" means a straight or branched alkenyl radical of, for example, 2 to 12 carbon atoms, such as 2, 3, 4, 5 or 6 carbon atoms, and containing one or more carbon-carbon double bonds and includes but is not limited to ethylene, n-propyl-1ene, n-propyl-2-ene, isopropylene etc.

"Alkynyl" relates to a straight or branched alkynyl radical of, for example, 2 to 12 carbon atoms, such as 2, 3, 4, 5 or 6 carbon atoms, and containing one or more triple bonds.

"Cyclohydrocarbyl" relates to a saturated, partly unsaturated or unsaturated 3 – 10, for example, 5, 6, 7, 8, 9 or 10, membered hydrocarbon ring, including cycloalkyl or aryl.

"Aryl" means an aromatic, for example, 6-10 membered hydrocarbon containing one, e.g. 6C-10C, ring which is optionally fused to one or more saturated or

unsaturated rings, including phenyl or phenyl substituted by an alkyl or alkoxy group in which alkyl and alkoxy are as described herein.

"Heteroary!" means an aromatic, for example, 5-10 membered aromatic ring containing one or more heteroatoms selected from N, O or S, and containing one ring which is optionally fused to one or more saturated or unsaturated rings.

"Heterocyclyl" means, for example, a 3-10 membered ring system containing one or more heteroatoms selected from N, O or S and includes heteroaryl. The heterocyclyl system may contain one ring or may be fused to one or more saturated or unsaturated rings; the heterocyclyl may be fully saturated, partially saturated or unsaturated.

"Cyclic group" means a ring or ring system, which may be unsaturated or partially unsaturated but is usually saturated, typically containing 5 to 13 ring-forming atoms, for example a 5- or 6- membered ring.

Examples of cyclohydrocarbyl or heterocyclyl groups include but are not limited to cyclohexyl, phenyl, acridine, benzimidazole, benzofuran, benzothiophene, benzoxazole, benzothiazole, carbazole, cinnoline, dioxin, dioxane, dioxolane, dithiane, dithiazine, dithiazole, dithiolane, furan, imidazole, imidazoline, imidazoline, indole, indoline, indolizine, indazole, isoindole, isoquinoline, isooxazole, isothiazole, morpholine, napthyridine, oxazole, oxadiazole, oxathiazole, oxathiazole, isothiazole, oxazine, oxadiazine, phenazine, phenothiazine, phenoxazne, phthalazine, piperazine, piperidine, pteridine, purine, putrescine, pyran, pyrazine, pyrazole, pyrazoline, pyrazolidine, pyridazine, pyridine, pyrimidine, pyrroliddine, pyrrole, pyrroline, quinoline, quinoxaline, quinazoline, quinnolizine, tetrahydrofuran, tetrazine, tetrazole, thiophene, thiadiazine, thiadiazole, thiatriazole, thiazine, thiazole, thiomorpholine, thianaphthalene, thiopyran, triazine, triazole, trithiane, tropine.

Halogen means F, Cl, Br, or I.

In one class of compounds R' and R'' are H. Compounds such as these having 1 R group and 3 hydrogens are referred to herein as primary ammonium ions.

The invention covers compounds of formula (I) having 2 R groups and 2 hydrogens and which are referred to herein as secondary ammonium ions respectively. The invention further covers compounds having 3 R groups and 1 hydrogen and which are referred to herein as tertiary ammonium ions.

Included is a class of compounds in which R' and R' are different and have the same meaning as R.

In one class of compounds, there are excluded cations where R, R' and R" are the same and are ethyl or butyl.

Where R' and R" are both CH₂, the invention may include the proviso that R is not H.

Where one or R' and R'' is H and the other is CH₃, the invention may include the proviso that R is not CH₃.

In addition to demonstrating high solvation capability, the ionic liquids of the present invention have a low viscosity, are non-toxic and are colourless. These features make the ionic liquids of the present invention useful as solvents in a variety of processes.

Preferably, R is substituted with a moiety selected from the group consisting of alkenyl, hydroxyl, amino, thio, carbonyl and carboxyl groups. More preferably, R is substituted with a hydroxyl, amino, thiol moiety.

If more than one substituent group (for example, selected from the group consisting of alkenyl, hydroxyl, amino, thiol, carbonyl and carboxyl groups) is present then more than one substituent group may be present on a single cation.

In one class of compounds, R is a hydroxyalkyl group having 1, 2, 3, 4, 5 or 6 C atoms. The hydroxyalkyl group may have a hydroxyl moiety on its free, terminal carbon. R may be a polyol having 2 to 6 C atoms, for example, a di-alkanol, tri-alkanol or tetra-alkanol group. More preferably, the cation is an ethanolammonium, diethanolammonium or triethanolammonium ion.

In another class of compounds, R is an aminoalkyl group having 2 to 8 C atoms, for example, 2, 3, 4, 5, 6, 7 or 8 C atoms. The aminoalkyl may be a di or tri-aminoalkyl group.

In some compounds, R is putrescine, pyrrole, piperidine, tropine or cyclohexane.

Preferred cations include an ethanolammonium. diethanolammonium, butyldiethanolammonium, dimethylethanolammonium, putrescinium. 1-(3hydroxypropyl)putrescinium, N-methylcyclohexylammonium, N-(3-hydroxypropyl)-N-methylcyclohexylammonium, N-methylpyrrolidinium N-(3-hydroxypropyl)-Nmethylpyrrolidinium, 3-methylpiperidinium, N-(3-hydroxypropyl)-3methylpiperidinium. N-methylpiperidinium, N-(3-hydroxypropyl)-Nmethylpiperidinium, tropinium, pyridinium, N-(3-hydroxypropyl)pyridinium, 3hydroxypyridinium, N-(3-hydroxypropyl)-3-hydroxypytidinium or N-butyl-3hydroxypyridinium cation.

Any anion included in the above list may be combined with any disclosed cation.

The identity of the anions in the ionic liquids of the invention is not critical. The only theoretical constraint upon the choice of the anion is its ionic weight in order to keep the melting point of the ionic liquid below the desired temperature.

Preferably the anion is selected from halogenated inorganic anions, nitrates, sulphates, phosphates, carbonates, sulphonates and carboxylates. The sulphonates and carboxylates may be alkylsulphonates and alkylcarboxylates, in which the alkyl group is a moiety, for example having 1 to 20 C atoms, selected alkyl and alkyl substituted at any position with alkenyl, alkoxy, alkeneoxy, aryl, arylalkyl, aryloxy, amino, aminoalkyl, thio, thioalkyl, hydroxyl, hydroxyalkyl, carbonyl, oxoalkyl, carboxyl, carboxyalkyl or halide function, including all salts, ethers, esters, pentayalent nitrogen or phosphorus derivatives or stereoisomers thereof. example, the anion may be selected from chloride, iodide, hexafluorophosphate, tetrafluoroborate, trifluoroacetate, benzoate, salicylate, ± -lactate, (-) lactate, (+) pantothenate, (±) -tartrate, (+) -tartrate, (-) -tartrate, (±) -hydrogen tartrate, (+) hydrogen tartrate, (-) -hydrogen tartrate, (±) -potassium tartrate, (+) -potassium tartrate, (-) -potassium tartrate, meso-tartrate, meso-1-hydrogen tartrate, meso-2hydrogen tartrate, meso-1-potassium tartrate, meso-2-potassium tartrate. especially preferred anion is an organic carboxylate. When the anion is required to include a labile proton then tartrate and lactate functional groups are preferred. Both tartrate and lactate comprise acid and hydroxyl functional groups.

The ionic liquid according to the invention may contain cations which are all the same or which are different. In the same way, the ionic liquids may contain anions which are all the same or which are different. Thus the invention encompasses ionic liquids including a mixture of different cations and/or different anions.

Ionic liquids of the invention may include any of the following:
Ethanolammonium methanesulfonate
Ethanolammonium glycolate
Diethanolammonium hydrogen carbonate
Diethanolammonium hexafluorophosphate
Diethanolammonium methanesulfonate
Diethanolammonium hydrogen sulfate

Diethanolammonium dihydrogen phosphate

Diethanolammonium formate

Diethanolammonium glycolate

Diethanolammonium crotonate

Diethanolammonium dihydrogen borate

Diethanolammonium trifluoroacetate

Diethanolammonium benzoate

Diethanolammonium salicylate

Diethanolammonium (±)-lactate

Diethanolammonium (±)-hydrogen tartrate

Diethanolammonium hydrogen oxalate

Diethanolammonium phenylacetate

Di(diethanolammonium) carbonate

Di(diethanolammonium) sulfate

Di(diethanolammonium) hydrogen phosphate

Di(diethanolammonium) (±)-tartrate

Di(diethanolammonium) oxalate

Di(diethanolammonium) hydrogen borate

Butyldiethanolammonium hydrogen carbonate

Butyldiethanolammonium hexafluorophosphate

Butyldiethanolammonium methanesulfonate

Butyldiethanolammonium hydrogen sulfate

Butyldiethanolammonium dihydrogen phosphate

Butyldiethanolammonium formate

Butyldiethanolammonium benzoate

Butyldiethanolammonium salicylate

Butyldiethanolammonium glycolate

Butyldiethanolammonium (±)-lactate

Butyldiethanolammonium (+)-lactate

Butyldiethanolammonium (-)-lactate

Butyldiethanolammonium hydrogen oxalate

Butyldiethanolammonium crotonate

Butyldiethanolammonium nicotinate

Butyldiethanolammonium acetylsalicylate

Butyldiethanolammonium iodide

Di(butyldiethanolammonium) carbonate

Di(butyldiethanolammonium) sulfate

Di(butyldiethanolammonium) hydrogen phosphate

Di(butyldiethanolammonium) (±)-tartrate

Di(butyldiethanolammonium) oxalate

Dimethylethanolammonium methanesulfonate

Dimethylethanolammonium hydrogen sulfate

Dimethylethanolammonium dihydrogen phosphate

Dimethylethanolammonium formate

Dimethylethanolammonium salicylate

Dimethylethanolammonium glycolate

Dimethylethanolammonium (±)-lactate:

Dimethylethanolammonium hydrogen oxalate

Di(dimethylethanolammonium) sulfate

Di(dimethylethanolammonium) hydrogen phosphate

Di(dimethylethanolammonium) oxalate

Putrescinium mono(methanesulfonate)

Putrescinium mono(glycolate)

Putrescinium mono[(±)-lactate]

Di(putrescinium) mono(hydrogen phosphate)

Di(putrescinium) mono[(±)-tartrate]

Di(putrescinium) mono(hydrogen borate)

Putrescinium di(methanesulfonate)

Putrescinium di(glycolate)

1-(3-Hydroxypropyl)putrescinium mono(methanesulfonate)

1-(3-Hydroxypropyl)putrescinium mono(hydrogen sulfate)

1-(3-Hydroxypropyl)putrescinium mono(glycolate)

- Di[1-(3-hydroxypropyl)putrescinium] sulfate
- N-Methylcyclohexylammonium methanesulfonate
- N-Methylcyclohexylammonium glycolate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium formate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium salicylate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium glycolate
- Di[N-(3-hydroxypropyl)-N-methylcyclohexylammonium] sulfate
- N-Methylpyrrolidinium methanesulfonate
- N-Methylpytrolidinium glycolate
- N-(3-Hydroxypropyl)-N-methylpyrrolidinium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylpyrrolidinium glycolate
- 3-Methylpiperidinium methanesulfonate
- 3-Methylpiperidinium glycolate
- N-(3-Hydroxypropyl)-3-methylpiperidinium methanesulfonate
- N-(3-Hydroxypropyi)-3-methylpiperidinium glycolate
- N-Methylpiperidinium methanesulfonate
- N-Methylpiperidinium glycolate
- N-(3-Hydroxypropyl)-N-methylpiperidinium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylpiperidinium glycolate
- Tropinium methanesulfonate
- N-(3-Hydroxypropyl)pyridinium hexafluorophosphate
- N-(3-Hydroxypropyl)pyridinium methanesulfonate
- N-(3-Hydroxypropyl)pyridinium glycolate
- 3-Hydroxypyridinium methanesulfonate
- 3-Hydroxypyridinium glycolate
- 3-Hydroxypyridinium (±)-lactate
- N-(3-Hydroxypropyi)-3-hydroxypyridinium methanesulfonate
- N-(3-Hydroxypropyl)-3-hydroxypyridinium glycolate
- N-Butyl-3-hydroxypyridinium methanesulfonate
- N-Butyl-3-hydroxypyridinium glycolate

The term "ionic liquid" herein includes, but is not limited to, compounds composed of ions and liquid at temperatures at which the compound is stable and the ionic liquids may have a melting point below 30°C, for example, below 25°C and optionally below 20°C. The boiling point of the ionic liquid may be at least 200°C. It may be above 500°C or even above 1000°C.

According to a further aspect, the present invention provides a process for the preparation of an ionic liquid according to the invention, the process comprising the steps of:

- i.) providing an organic primary, secondary or tertiary amine; and
- ii.) neutralising the compound in (i) with an acid.

The process according to the invention may comprise the steps of:

i.) providing a nitrogen-containing compound of the formula (II)

NRR'R" (II)

in which R, R' and R" have the meaning defined herein; and

ii.) neutralising the compound in (i) with an acid.

The process of the present invention provides an economical route to the manufacture of ionic liquids since the process involves only a single step and uses starting materials that are generally readily available.

During the process of the invention, the nitrogen atom of the primary, secondary or tertiary amine is protonated to provide a protonated ammonium ion.

Preferably, the acid includes an anion as defined herein.

Preferably the acid anion comprises a halogenated inorganic anion, nitrate, sulphate, carbonate, sulphonate or carboxylate.

The invention also encompasses compounds of formula (II) and their use in the preparation of one or more ionic liquids.

The invention further provides the use of a cation as defined in the ionic liquids of the present invention in a solvent for enzyme-catalysed reactions. Further provided is the use of an ionic liquid according to the present invention as a solvent for enzyme-catalysed reactions.

The use of ionic liquids in certain biological and/or chemical reactions has several advantages over traditional aqueous solutions. Ionic liquids have an ability to dissolve a wide range of inorganic, organic, polymeric and biological materials, often to a very high concentration. They have a wide liquid range, allowing both high and low temperature processes to be carried out in the same solvent. They do not elicit solvolysis phenomena and most stabilise short-lived reactive intermediates. There are no pH effects in the solvents and there is practically zero vapour pressure over much of the liquid range. Ionic liquids also exhibit excellent electrical and thermal conductivity whilst being non-flammable, recyclable and generally of low toxicity.

The invention further provides the use of an ionic liquid, or of a cation as defined in an ionic liquid, according to the present invention in a solvent for organic synthesis, matrixes in matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry, solvent extraction (e.g to remove desired components from an immicible liquid or solid) or gas chromatography, catalysis, liquefaction, nuclear fuel reprocessing, fuel cells, electrochemical applications, pervaporation, drug delivery, lubrication.

Further provided is a method for carrying out an enzyme-catalysed reaction comprising

- i.) providing a liquid reaction medium which comprises an ionic liquid according to the present invention;
- ii.) providing in the liquid reaction medium an enzyme and a substrate for the enzyme; and
- iii.) allowing reaction of the substrate to occur.

Further provided is a method for the synthesis of one or more organic compounds, the method comprising carrying out an organic synthesis reaction in an ionic liquid according to the present invention.

The invention will now be described by way of the following, non-limiting example:

MATERIALS AND METHODS

Preparation of ammonium-based ionic liquids bearing one or more ammoniacal protons

The requisite stoichiometric equivalents of the parent amine and complementary acid were dissolved independently in water, to give solutions of relatively equal concentration. Equal volumes of these two solutions were mixed together in a flask, with stirring and cooling, at a rate sufficiently slow as to prevent the temperature of the reaction from exceeding 60°C. When neutralization was complete, the excess water was removed *in vacuo*, at temperatures not exceeding 60°C. The product was then freeze-dried, analysed and stored in a desiccated condition.

Preparation of diethanolammonium sulfate

Aqueous solutions of diethanolamine (100.00 mL, 2.000M concentration) and sulfuric acid (50.00 mL, 2.000 M concentration) were mixed together in a 250mL flask, with stirring and cooling. After neutralization was complete, the cold aqueous

solution was filtered, transferred to a fresh flask and the excess water removed on a rotary evaporator. The sample was then frozen and dried in vacuo, being allowed to rise gradually to room temperature. The product was analysed by FT-IR, UV-Vis and 1H-NMR spectroscopy and elemental analysis; water content was determined by means of the Karl Fischer titration and the purified material was stored over

anhydrous calcium chloride in a vacuum oven, at a temperature of 50°C.

CLAIMS

- 1. An ionic liquid comprising an anion and a cation wherein the cation is a primary, secondary or tertiary ammonium ion containing a protonated nitrogen atom.
- 2. An ionic liquid comprising an anion and a cation characterised in that the cation is a nitrogen-containing cation of the formula (I)

N'HRR'R" (I)

in which R is a hydrocarbyl group optionally substituted with by one or more substituents selected from nitrogen-containing functional groups (including nitrile, nitro or amino or another basic nitrogen-containing functional group), thiol, alkythio, sulphonyl, thiocyanate, isothiocyanate, azido, hydrazino, halogen, alkyl optionally interrupted by one or more ether or thioether linkages, alkoxy, alkenyl, hydroxy, carbonyl (including aldehyde or ketone), carboxyl, boronate, silyl and substituted amino (e.g. mono- or di-alkylamino or alkyamido); and

R' and R'', which may be the same or different, each represent H or R; or any two or three of R, R', R'' may be joined together with the N to form a cyclic group.

- 3. An ionic liquid as claimed in claim 2 wherein the hydrocarbyl is an alkyl, alkynyl or cyclohydrocarbyl group
- 4. An ionic liquid as claimed in claim 3 wherein the cyclohydrocarbyl is a cycloalkyl or cycloalkenyl.

- 5. An ionic liquid as claimed in any of claims 2 to 4 wherein the alkyl is methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl.
- 6. An ionic liquid as claimed in any of claims 2 to 4 wherein the alkyl group is substituted with one or more halogen atoms.
- 7. An ionic liquid as claimed in claim 4 wherein the cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.
- An ionic liquid as claimed in claim 2 wherein R' and R' are H.
- 9. An ionic liquid as claimed in claim 2 wherein R' and R" are different and have the same meaning as R.
- 10. An ionic liquid as claimed in claim 2 excluding cations in which R, R' and R'' are the same and are ethyl or butyl.
- 11. An ionic liquid as claimed in claim 2 including the proviso that when R' and R" are both CH₃, R is not H.
- 12. An ionic liquid as claimed in claim 2 including the proviso that when one of R' and R'' is H and the other is CH₃, R is not CH₃.
- 13. An ionic liquid as claimed in claim 2 wherein R is substituted with a moiety selected from the group consisting of alkenyl, hydroxyl, amino, thio, carbonyl and carboxyl groups.
- 14. An ionic liquid as claimed in claim 13 wherein R is substituted with a hydroxyl, amino or thiol moiety.

- 15. An ionic liquid as claimed in claim 2 wherein R is a hydroxyalkyl group having 1, 2, 3, 4, 5 or 6 C atoms.
- 16. An ionic liquid as claimed in claim 15 wherein the hydroxyalkyl group has a hydroxyl moiety on its free, terminal carbon.
- 17. An ionic liquid as claimed in claim 15 or 16 wherein R is a polyol having 2 to 6 C atoms.
- 18. An ionic liquid as claimed in claim 17 wherein R is a di-alkanol, tri-alkanol or tetra-alkanol group.
- 19. An ionic liquid as claimed in claim 1 or 2 wherein the cation is an ethanolammonium, diethanolammonium or triethanolammonium ion.
- 20. An ionic liquid as claimed in claim 2 wherein R is an aminoalkyl group having 2 to 8 C atoms
- 21. An ionic liquid as claimed in claim 20 wherein the aminoalkyl may be a di or tri-aminoalkyl group.
- 22. An ionic liquid as claimed in claim 2 wherein R is putrescine, pyrrole, piperidine, tropine or cyclohexane.
- 23. An ionic liquid as claimed in claim 1 or 2 wherein the cation is selected from the group consisting of an ethanolammonium, diethanolammonium, butyldiethanolammonium, dimethylethanolammonium, putrescinium, 1-(3hydroxypropyl)putrescinium, N-methylcyclohexylammonium, N-(3-hydroxypropyl)-N-methylcyclohexylammonium, N-methylpyrrolidinium N-(3-hydroxypropyl)-Nmethylpyrrolidinium, 3-methylpiperidinium, N-(3-hydroxypropyl)-3methylpiperidinium, N-methylpiperidinium, N-(3-hydroxypropyl)-N-

methylpiperidinium, tropinium, pyridinium, N-(3-hydroxypropyl)pyridinium, 3hydroxypyridinium, N-(3-hydroxypropyl)-3-hydroxypyridinium or N-butyl-3hydroxypyridinium cation.

- 24. An ionic liquid as claimed in claim 1 or 2 wherein the anion is selected from halogenated inorganic anions, nitrates, sulphates, phosphates, carbonates, sulphonates and carboxylates.
- 25. An ionic liquid as claimed in claim 24 wherein the sulphonates and carboxylates are alkylsulphonates and alkylcarboxylates respectively.
- 26. An ionic liquid as claimed in claim 25 wherein the alkyl group is a moiety selected from alkyl and alkyl substituted at any position with alkenyl, alkoxy, alkeneoxy, aryl, arylalkyl, aryloxy, amino, aminoalkyl, thio, thioalkyl, hydroxyl, hydroxyalkyl, carbonyl, oxoalkyl, carboxyl, carboxyalkyl or halide function
- 27. An ionic liquid as claimed in claim 24 wherein the anion is selected from chloride, iodide, hexafluorophosphate, tetrafluoroborate, trifluoroacetate, benzoate, salicylate, \pm -lactate, (-) lactate, (+) -pantothenate, (\pm) -tartrate, (+) -tartrate, (-) tartrate, (±) -hydrogen tartrate, (+) -hydrogen tartrate, (-) -hydrogen tartrate, (±) potassium tartrate, (+) -potassium tartrate, (-) -potassium tartrate, meso-tartrate, meso-1-hydrogen tartrate, meso-2-hydrogen tartrate, meso-1-potassium tartrate, meso-2-potassium tartrate.
- 28. An ionic liquid as claimed in claim 24 wherein the anion is an organic carboxylate.
- 29. An ionic liquid as claimed in claim 1 or 2 which is selected from the group consisting of:

Ethanolammonium methanesulfonate Ethanolammonium glycolate

Diethanolammonium hydrogen carbonate

Diethanolammonium hexafluorophosphate

Diethanolammonium methanesulfonate

Diethanolammonium hydrogen sulfate

Diethanolammonium dihydrogen phosphate

Diethanolammonium formate

Diethanolammonium glycolate

Diethanolammonium crotonate

Diethanolammonium dihydrogen borate

Diethanolammonium trifluoroacetate

Diethanolammonium benzoate

Diethanolammonium salicylate

Diethanolammonium (±)-lactate

Diethanolammonium (±)-hydrogen tartrate

Diethanolammonium hydrogen oxalate

Diethanolammonium phenylacetate

Di(diethanolammonium) carbonate

Di(diethanolammonium) sulfate

Di(diethanolammonium) hydrogen phosphate

Di(diethanolammonium) (±)-tartrate

Di(diethanolammonium) oxalate

Di(diethanolammonium) hydrogen borate

Butyldiethanolammonium hydrogen carbonate

Butykliethanolammonium hexafluorophosphate

Butyldiethanolammonium methanesulfonate

Butyldiethanolammonium hydrogen sulfate

Butyldiethanolammonium dihydrogen phosphate

Butyldiethauolammonium formate

Butyldiethanolammonium benzoate

Butyldiethanolammonium salicylate

Butyldiethanolammonium glycolate

Butyldiethanolammonium (±)-lactate

Butyldiethanolammonium (+)-lactate

Butyldiethanolammonium (-)-lactate

Butyldiethanolammonium hydrogen oxalate

Butyldiethanolammonium crotonate

Butyldiethanolammonium nicotinate

Butyldiethanolammonium acetylsalicylate

Butyldiethanolammonium iodide

Di(butyldiethanolammonium) carbonate

Di(butyldiethanolammonium) sulfate

Di(butyldiethanolammonium) hydrogen phosphate

Di(butyldiethanolammonium) (±)-tartrate

Di(butyldiethanolammonium) oxalate

Dimethylethanolammonium methanesulfonate

Dimethylethanolammonium hydrogen sulfate

Dimethylethanolammonium dihydrogen phosphate

Dimethylethanolammonium formate

Dimethylethanolammonium salicylate

Dimethylethanolammonium glycolate

Dimethylethanolammonium (±)-lactate

Dimethylethanolammonium hydrogen oxalate

Di(dimethylethanolammonium) sulfate

Di(dimethylethanolammonium) hydrogen phosphate

Di(dimethylethanolammonium) oxalate

Putrescinium mono(methanesulfonate)

Putrescinium mono(glycolate)

Putrescinium mono[(±)-lactate]

Di(putrescinium) mono(hydrogen phosphate)

 $\mathbf{D}i(\text{putrescinium}) \text{ mono}[(\pm)\text{-tartrate}]$

Di(putrescinium) mono(hydrogen borate)

Putrescinium di(methanesulfonate)

Putrescinium di(glycolate)

- 1-(3-Hydroxypropyl)putrescinium mono(methanesulfonate)
- 1-(3-Hydroxypropyl)putrescinium mono(hydrogen sulfate)
- 1-(3-Hydroxypropyl)putrescinium mono(glycolate)
- Di[1-(3-hydroxypropyl)putrescinium] sulfate
- N-Methylcyclohexylammonium methanesulfonate
- N-Methylcyclohexylammonium glycolate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium formate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium salicylate
- N-(3-Hydroxypropyl)-N-methylcyclohexylammonium glycolate
- Di[N-(3-hydroxypropyl)-N-methylcyclohexylammonium] sulfate
- N-Methylpyrrolidinium methanesulfonate
- N-Methylpyrrolidinium glycolate
- N-(3-Hydroxypropyl)-N-methylpyrrolidinium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylpyrrolidinium glycolate
- 3-Methylpiperidinium methanesulfonate
- 3-Methylpiperidinium glycolate
- N-(3-Hydroxypropyl)-3-methylpiperidinium methanesulfonate
- N-(3-Hydroxypropyl)-3-methylpiperidinium glycolate
- N-Methylpiperidinium methanesulfonate
- N-Methylpiperidinium glycolate
- N-(3-Hydroxypropyl)-N-methylpiperidinium methanesulfonate
- N-(3-Hydroxypropyl)-N-methylpiperidinium glycolate
- Tropinium methanesulfonate
- N-(3-Hydroxypropyl)pyridinium hexafluorophosphate
- N-(3-Hydroxypropyl)pyridinium methanesulfonate
- N-(3-Hydroxypropyl)pyridinium glycolate
- 3-Hydroxypyridinium methanesulfonate
- 3-Hydroxypyridinium glycolate
- 3-Hydroxypyridinium (\pm)-lactate

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N-(3-Hydroxypropyl)-3-hydroxypyridinium methanesulfonate N-(3-Hydroxypropyl)-3-hydroxypyridinium glycolate N-Butyl-3-hydroxypyridinium methanesulfonate and N-Butyl-3-hydroxypyridinium glycolate

- A process for the preparation of an ionic liquid as claimed in claim 1 or 2, the **3**Q. process comprising the steps of:
 - providing an organic primary, secondary or tertiary amine; and ii.)
 - neutralising the compound in (i) with an acid. ii.)
- A process as claimed in claim 30 which comprises the steps of: 31.
 - providing a nitrogen-containing compound of the formula (II) i.)

(II) NRR'R''

in which R is a hydrocarbyl group optionally substituted with by one or more substituents selected from nitrogen-containing functional groups (including nitrile, nitro or amino or another basic nitrogen-containing functional group), thiol, alkythio, sulphonyl, thiocyanate, isothiocyanate, azido, hydrazino, halogen, alkyl optionally interrupted by one or more ether or thioether linkages, alkoxy, alkenyl, hydroxy, carbonyl (including aldehyde or ketone), carboxyl, boronate, silyl and substituted amino (e.g. mono- or di-alkylamino or alkyamido); and

R' and R'', which may be the same or different, each represent H or R; or

any two or three of R, R', R'' may be joined together with the N to form a cyclic group; and

- iii.) neutralising the compound in (i) with an acid.
- 32. A process as claimed in claim 30 or 31 wherein the acid includes an anion comprising a halogenated inorganic anion, nitrate, sulphate, carbonate, sulphonate or carboxylate.
- 33. The use of an ionic liquid as claimed in any claims 1 to 29 as a solvent for enzyme-catalysed reactions.
- 34. The use of an ionic liquid as claimed in any of claims 1 to 29 in a solvent for organic synthesis, matrixes in matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry, solvent extraction, gas chromatography, catalysis, liquefaction, nuclear fuel reprocessing, fuel cells, electrochemical applications, pervaporation, drug delivery or lubrication.
- 35. A method for carrying out an enzyme-catalysed reaction comprising
 - iv.) providing a liquid reaction medium which comprises an ionic liquid as claimed in any of claims 1 to 29;
 - v.) providing in the liquid reaction medium an enzyme and a substrate for the enzyme; and
 - vi.) allowing reaction of the substrate to occur.

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